

CHARACTERISTICS AND SOURCES OF PM_{2.5} IN THE PITTSBURGH REGION

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Abstract

This paper describes results from the Pittsburgh Air Quality Study (PAQS), a large-scale ambient air quality study focused on ambient particulate matter in the Pittsburgh and Upper Ohio River Valley Region. PAQS is a collaborative project involving 20 research groups. Ambient measurements are made at a central supersite located in an urban neighborhood within Pittsburgh, and satellite sites both within the city of Pittsburgh and the surrounding region. A wide array of standard and advance aerosol instrumentation is deployed at the central site including integrated samplers, semi continuous instruments, and single particle instruments. This talk summarizes some important initial results from the PAQS, focusing on the characteristics and the sources of the fine particulate matter in the Pittsburgh region during the summer of 2001.

During the summer of 2001 the average PM_{2.5} mass concentration in Pittsburgh was around 24 $\mu\text{g}/\text{m}^3$ with the major components being sulfate (40% of total mass) and organic material (24% of total mass). The PM_{2.5} mass in the Pittsburgh region is dominated by regional transport, with levels varying in an episodic fashion driven largely by meteorology. Secondary organic aerosol is estimated to contribute between 20 and 40% of the PM_{2.5} organic mass. On a number basis the particle size distribution is dominated by ultrafine aerosol. Important sources of ultrafine aerosol include mobile sources and nucleation. The data from the PAQS reveal frequent nucleation events in which large numbers of ultrafine particles are created by gas to particle conversion processes. These events typically occur in the late morning on relatively clean, sunny days; the fresh aerosol grows in size over the course of the day due to coagulation and condensation.

Introduction

Airborne particulate matter (PM) includes both organic and inorganic components and is formed from a variety of sources, including combustion, dust, and particle formation from oxidation of precursor gases. Epidemiological studies have shown adverse health effects of PM including respiratory irritation and changes in pulmonary function as well as associations between PM mass concentrations and mortality [1]. Some studies have also shown that ultrafine particles (less than 100 nm diameter) are likely to cause adverse health effects [2-4]. In addition to affecting human health, fine particulate matter impacts climate and visibility. Because of these effects, sources of fine PM and secondary PM precursors are increasingly regulated. A good understanding of emission sources and atmospheric processes that govern

fine PM concentrations and size distributions is critical to the design of effective control policies.

This paper uses field results from the Pittsburgh Air Quality Study to address three important questions regarding particulate matter in the Northeastern United States: (1) relative contribution of local versus regional sources; (2) quantification of carbonaceous aerosol concentrations with emphasis on the ratio of primary and secondary organic carbon; and (3) the formation of new particles through *in situ* nucleation.

Background

The Pittsburgh Air Quality Study (PAQS) is a hypothesis-driven multidisciplinary air pollution study designed to characterize fine particulate matter around Pittsburgh, evaluate next-generation aerosol monitoring instrumentation, elucidate source-receptor relationships, and improve understanding of atmospheric processes governing aerosol concentrations.

The measurement program features a central site located in Pittsburgh and a set of satellite sites (see Figure 1). Baseline monitoring began in June 2001 and will continue through the summer of 2002. Measurements include detailed characterization of PM size, surface, and volume distributions, size-resolved bulk chemical composition, continuous size-resolved single-particle composition measurements, organic aerosol speciation, measurement of the distribution and composition of ultrafine aerosols, semi-continuous measurements of metals, nitrate, sulfate, and aerosol carbon, measurements of bioaerosols, aerosol precursors, cloud and fog composition in the area, aerosol optical and hygroscopic properties, and meteorological variables. Intensive sampling periods were conducted in July 2001 and January 2002 to examine temporal variations and to collect detailed data for model testing and validation. The data from this project will be made available through an easily accessible electronic database.

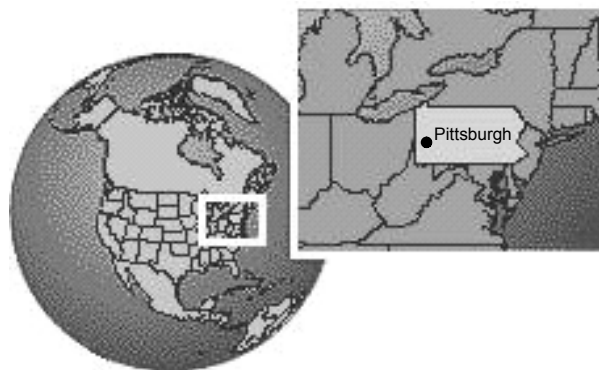


Figure 1. Map showing location of Pittsburgh Air Quality Study

Results Overview: PM_{2.5} Levels, Composition, Transport, and Meteorology

The average PM_{2.5} level measured for the first 7 months of the PAQS was 17 µg/m³, with higher levels during summer than winter. A summary of data is shown in Table 1. The summertime composition is dominated by organic carbon and sulfate, while wintertime composition is dominated by organic carbon, sulfate, and nitrate.

TABLE 1. Summary of Average Measurements from the Pittsburgh Air Quality Study

Parameter	Summer Intensive (July 2001)	Winter Intensive (January 2002)
PM _{2.5} (µg/m ³)	24	11
Temperature (°C)	22.8	3.0
Relative Humidity (%)	66	68
Average UV (W/m ²)	7.8	2.0
PM _{2.5} Sulfate (µg/m ³)	7.6	3.6
PM _{2.5} Nitrate (µg/m ³)	0.5	2.2
PM _{2.5} Organic Carbon (µg/m ³) ¹	7.9	4.7
PM _{2.5} Elemental Carbon (µg/m ³)	0.8	0.4

Regional-scale meteorology had a strong influence on ambient mass concentrations. Highest concentration periods occurred during stagnant warm periods of high pressure and low wind speeds. Concentrations of sulfate, nitrate, and organic carbon showed minimal diurnal pattern on average, suggesting that concentrations of these components are dominated by regional transport and meteorology. Concentrations of elemental carbon showed somewhat more diurnal variation, suggesting significant local source contributions.

Evidence of the Regional Contribution

Methods

During the month of July 2001, filter samplers were operated at the central supersite located in an urban park next to the Carnegie Mellon University campus in Pittsburgh. Samples were also collected at four satellite sites: Lawrenceville, Hazelwood, Florence and Greensburg. Lawrenceville and Hazelwood are located within a few kilometers of the main site, both in heavily populated areas of the city with considerable automobile traffic. The Florence site is located about 50 kilometers west of the main site in a rural area with no nearby sources. The Greensburg site is about 50 kilometers east of the main site in a suburban area, close to a

¹ Undenuded quartz filter with multiplier of 1.8 µg OC / µg Carbon

heavily traveled road but otherwise in an area of only moderate traffic with fewer stationary sources than in the city. By comparing how concentrations change at sites within Pittsburgh and at satellite sites much further from Pittsburgh, it is possible to identify the relative importance of local sources.

Results and Discussion

Figure 2 shows 24-hour average airborne concentrations of $PM_{2.5}$ mass determined gravimetrically using Teflon filters at the five monitoring sites during the summer 01 intensive. The $PM_{2.5}$ concentrations show considerable variability from day to day, which is most likely caused for the most part by changing meteorology. Note that concentrations track each other well among these five sites, with similar levels at the two rural sites (Florence and Greensburg) and at the three urban sites. This suggests that $PM_{2.5}$ mass at all five sites is determined mostly by the same sources, namely regional sources upwind of this area.

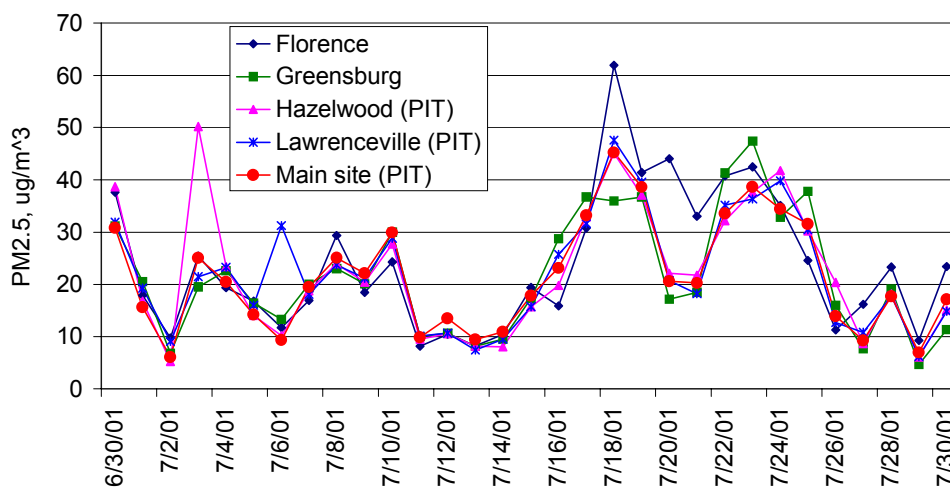


Figure 2. Time series of $PM_{2.5}$ mass measured at the central monitoring site and 4 satellite sites.

A similar finding is seen for airborne $PM_{2.5}$ sulfate, shown in Figure 3. In fact, the points at the five sites show closer agreement for sulfate than for $PM_{2.5}$ mass, suggesting that sulfate is influenced to a greater extent by regional sources upwind. This is a reasonable hypothesis since sulfate is known to be primarily a secondary pollutant that is influenced by sulfur emissions at least several hours transport time upwind. These emissions are mostly SO_2 . $PM_{2.5}$ mass, although containing a large fraction of sulfate, also contains other chemical species that may have local components in the city of Pittsburgh.

One example of a chemical species with a measurable local component is $PM_{2.5}$ nitrate, shown in Figure 4. On some days, the concentrations of nitrate at Florence and Greensburg are noticeably smaller than concentrations at the three urban sites. Florence, the most remote site, has the lowest concentration of the five sites on the majority of days during July.

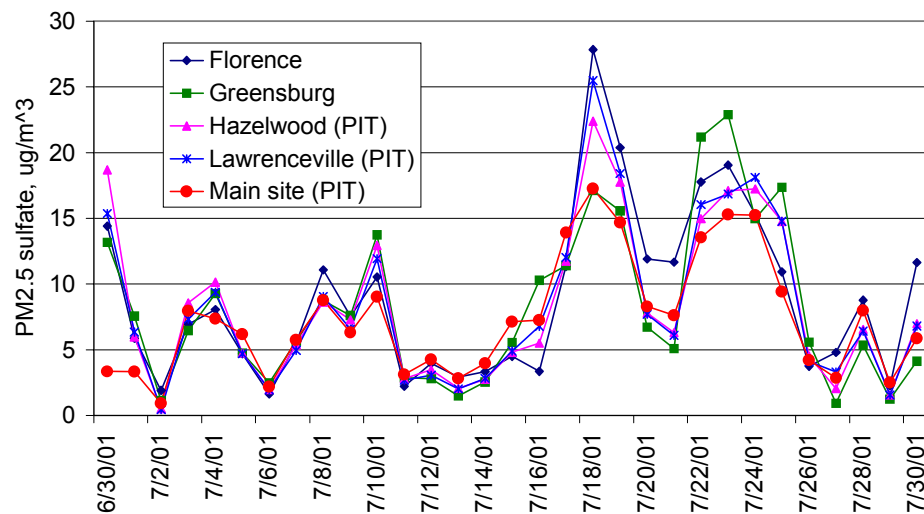


Figure 3. Time series of PM_{2.5} sulfate measured at the central monitoring site and 4 satellite sites.

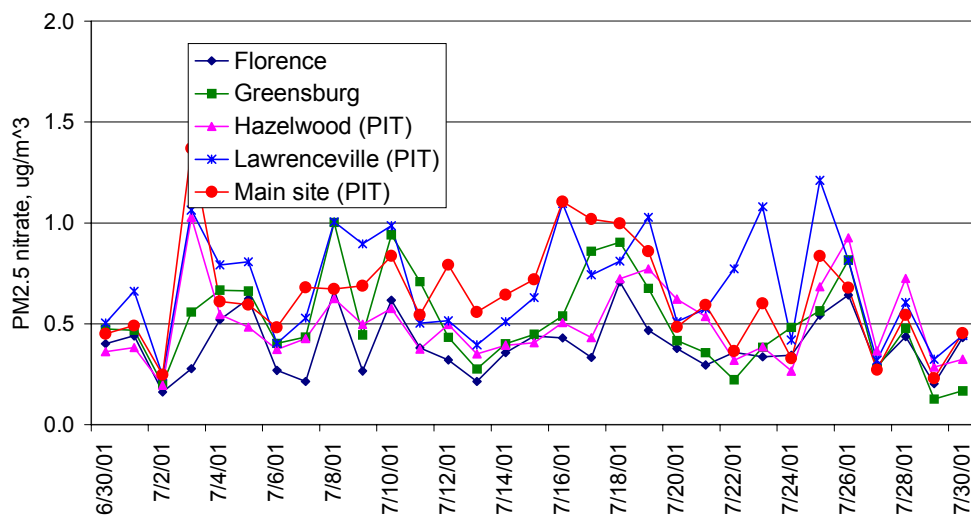


Figure 4. Time series of PM_{2.5} nitrate measured at the central monitoring site and 4 satellite sites.

ORGANICS

A major component of $PM_{2.5}$ in the Eastern US is carbonaceous material. Organic particulate matter results from both direct emissions from sources such as automobiles, trucks and industries (primary), and from the oxidation of organic gases (secondary). Data from the Pittsburgh Air Quality Study are used to examine the contribution of secondary organic aerosol to the total organic aerosol loading measured in the city during 2001 and 2002.

Carbonaceous Aerosol Sampling and Analysis

The Pittsburgh Air Quality Study (PAQS) operated three different samplers, shown in Figure 5, for collecting carbonaceous aerosol (one undenuded line and two denuded samplers). During the summer intensive (July-August 2001), an undenuded line and the denuded in-situ analyzer operated at high resolution sampling times (2-6 hrs), and another denuded line collected daily samples. During the regular sampling schedule (August 2001- April 2002), daily samples were collected on the undenuded sampler and 2-4 hrs samples were collected on the denuded in-situ analyzer.

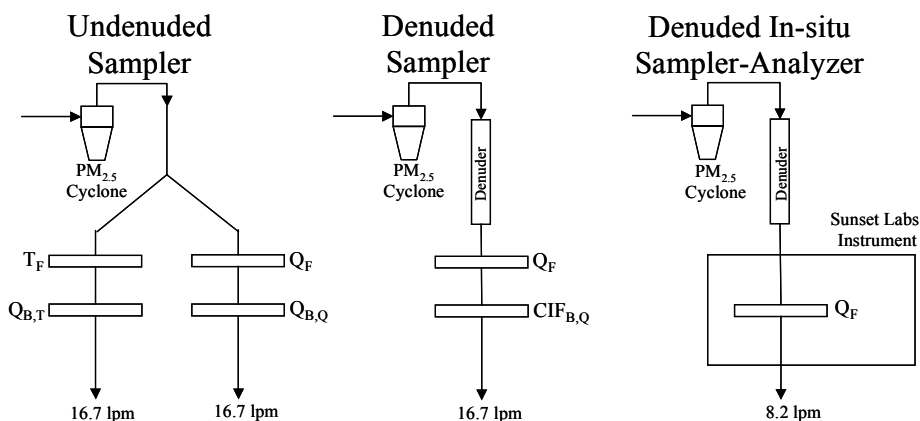


Figure 5. Schematic of the Pittsburgh Air Quality Study carbonaceous aerosol samplers. Subscript "F" denotes the front filter in the samplers. Backup filters are indicated as a subscript "B" followed by the type of filter they are after (T =Teflon, Q= quartz).

The contribution of secondary organic aerosol can be estimated by using elemental carbon as a tracer for primary emissions of organic particulate matter (OC to EC ratio approach). A systematic method for the determination of the primary ratio has been developed based on the correlation of measurements of OC and EC to gaseous tracers of photochemical activity (O_3) and primary emissions (CO , NO_x) [5].

This method is applied to different sets of organic aerosols measurements for carbonaceous concentrations at PAQS. Carbonaceous concentrations are classified into primary and secondary organic aerosol influenced, depending on their correlation to the tracers. Figure 6 shows the classification of points for two datasets of measurements obtained during the summer intensive at PAQS.

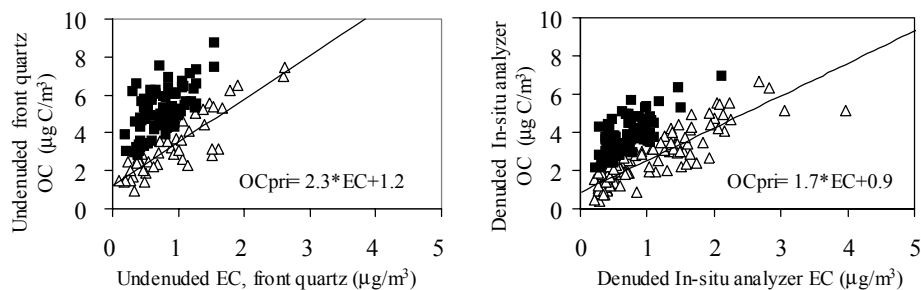


Figure 6. Carbonaceous concentrations influenced by primary emissions (open triangles) and SOA production (black squares) for high-resolution measurements (2-6 hrs samples) during the July intensive at the PAQS.

A linear regression by least squares minimization is fitted through the “primary” emissions influenced concentrations. The slope of the fit represents the OC to EC primary ratio and the intercept represents the “non-combustion organic carbon” contribution to the primary OC concentration. Consistent results for the SOA fraction are obtained when the method is applied to sets of measurements with different sampling artifact corrections for OC and EC.

Organic and Elemental Carbon Results

Figure 7 shows daily resolved OC composition for two of the different samplers at PAQS, during the summer intensive (July-August 2001). Overall, the results based on the two datasets are in a good agreement, predicting the same periods of SOA production for July.

Monthly averaged OC compositions for all three different samplers are shown in Figure 8. Similar results in the OC composition are obtained for all of the different measurements taken, applying the same approach to determine the primary OC to EC ratio and intercepts. In average, for July 2001, 30% of the OC consisted of SOA.

Figure 9 shows the monthly averaged concentrations of OC and EC for Pittsburgh during 2001 and 2002. The approach to determine the SOA contribution is applied on a monthly basis and estimates of the primary ratio and the non-combustion OC contribution are calculated. Figure 10 shows the fraction of SOA from the total OC concentration measured. This approach indicates that between 20 and 30% of the organic particulate matter in Pittsburgh during the summer and fall of 2001 is secondary in origin while negligible contributions of SOA are estimated for the winter of 2001-02.

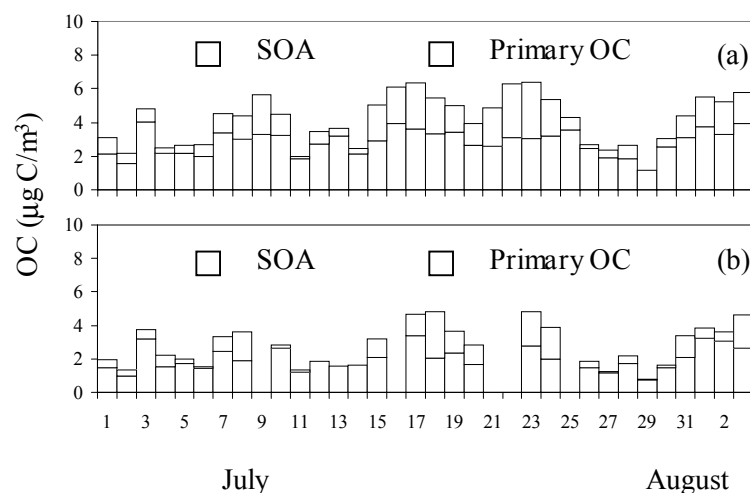


Figure 7. Daily averaged OC composition pattern during July, estimated from the high resolution measurements. SOA estimates were done with high-resolution parameters for the primary ratio and the non-combustion primary OC contribution. (a) Undenuded sampler using front quartz concentrations. (b) Concentrations from the denuded in-situ analyzer.

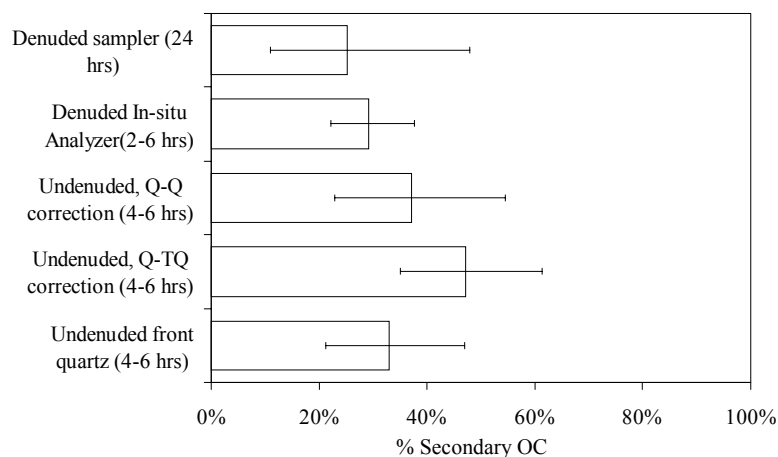


Figure 8. July monthly average SOA fraction of the Pittsburgh organic aerosol for all high-resolution datasets (2-6 hrs sampling times) and daily denuded sample (24 hrs). From all the datasets; in average 35 to 50% contribution of SOA is calculated for Pittsburgh in July 2001.

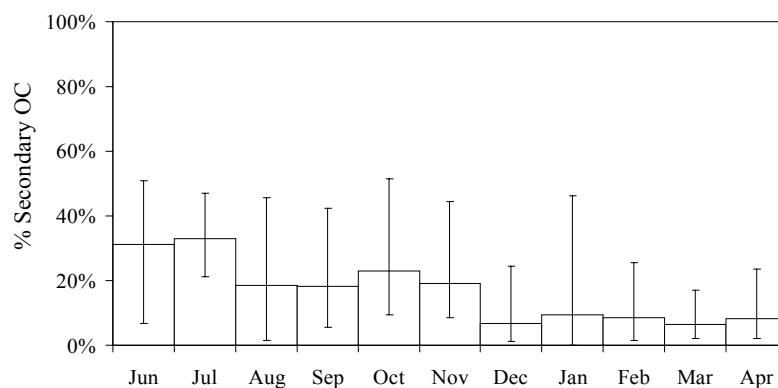


Figure 9. Monthly averaged carbonaceous aerosol concentrations for PAQS. Undenuded sampler, front quartz data.

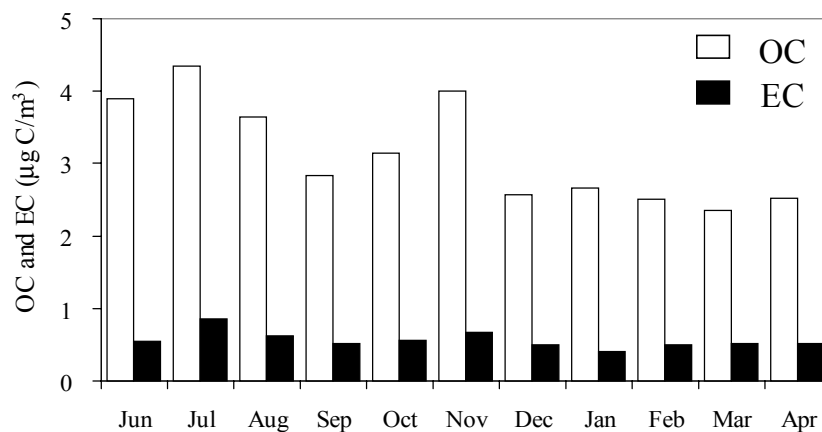


Figure 10. Monthly fraction contribution of SOA to the total OC concentration for PAQS. Undenuded sampler, front quartz data.

Nucleation and Ultrafine Particles

Methods

Two SMPS systems (TSI 3936R10 and TSI 3936N25) were operated at the main location continuously beginning in June of 2001. These instruments measured the size distribution of particles from 3 nm to 600 nm. Another SMPS system (TSI 3071/3010) was located at a

rural site in Florence, Pennsylvania, 38 km west (upwind) of the city during 2002. At each location, 8 size distributions were measured each hour.

Results and Discussion

From 30 to 50 percent of the study days were characterized by nucleation events. The events varied in intensity from weak increases in the ultrafine and nuclei mode particle counts to intense events, which increased the overall number concentration from less than 20,000 per cm^3 to over 100,000 per cm^3 in a few hours. The average number count and overall number distribution were heavily influenced by nucleation. For the summer intensive period, the hourly average concentration on days without nucleation activity was $15,500 \pm 800$ (95% confidence interval on mean). On days with nucleation this value was $21,200 \pm 1,600$, a 37% increase in average number concentration. These averages include all hours of the day, not just the few hours during which nucleation may occur.

In general, nucleation events corresponded with bright sun and low concentrations of preexisting aerosol. Clean, sunny, and cool conditions occurring after the passage of cold fronts usually showed nucleation. Some nucleation events were well correlated with high concentrations of sulfur dioxide. Other nucleation events happened within an hour of the breakup of overnight inversion layer, perhaps suggesting that the dilution of the pollutants in the mixed layer facilitated the formation of new particles.

Data from SMPS systems operating at the main urban site in Pittsburgh, and a rural site 38 km upwind showed that most of the events appear to occur over a large area and are not directly related to the emissions from the urban area. A comparison of data between the two sites on one specific day is shown in Figure 11, showing significant similarity between the two events.

Figure 12 compares the diurnal pattern of total particle number concentration for days with and without nucleation events. The frequency and intensity of these nucleation bursts make them the single biggest factor in determining the number concentration of particles at the sampling site in Schenley Park, followed by traffic intensity, other local combustion, and regional transport as contributing factors.

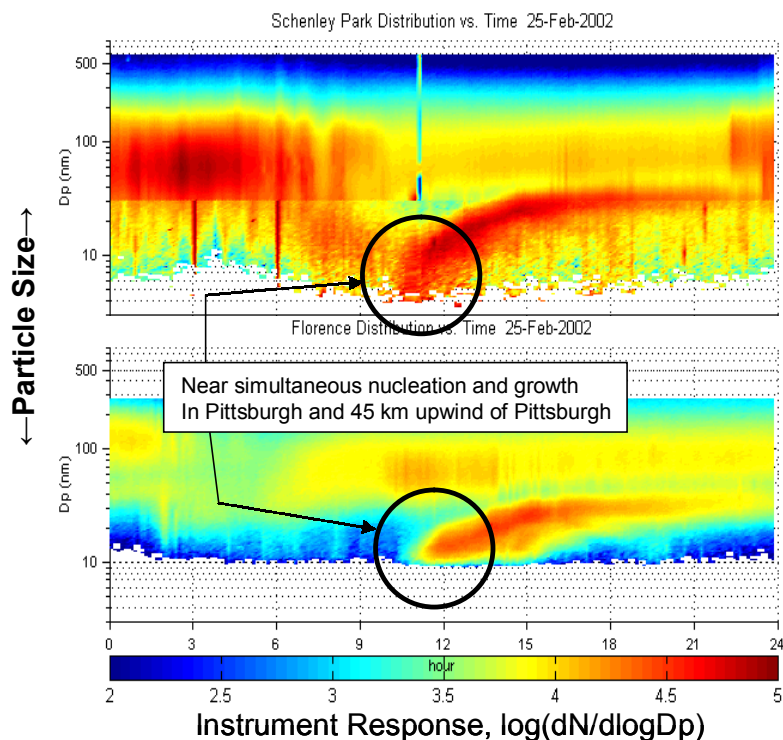


Figure 11. Comparison of measurements for February 25 from the Schenley Park (urban) site and Florence, PA (upwind, rural). The simultaneous nucleation at both sites has been seen several times since the Florence monitor was brought online in late February. This indicates a regional cause of the nucleation bursts.

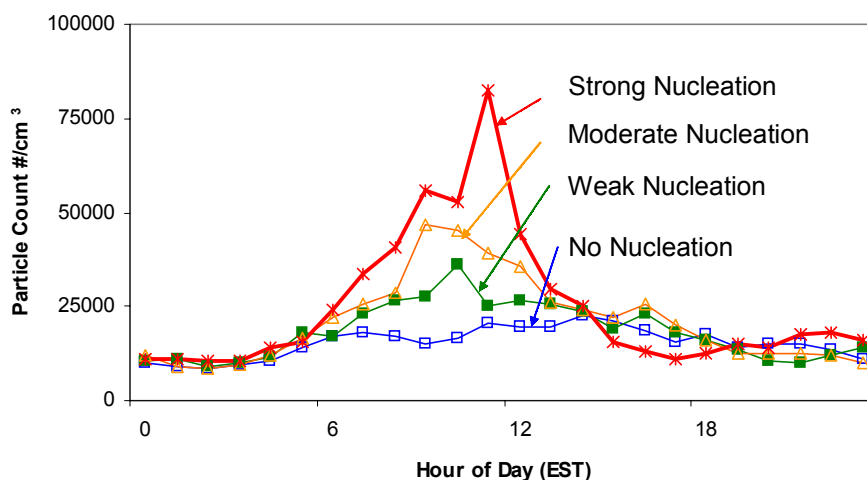


Figure 12. Total particle number concentration as a function of time of day for strong, moderate, weak, and no nucleation cases. Data is for the Schenley Park sampling station during July.

To date, three approaches have been taken to elucidate the chemical composition of the initial nuclei. Under consideration for nuclei composition are a binary mixture of sulfuric acid and water; a ternary mixture of sulfuric acid, water, and ammonium; and low vapor pressure organics.

In the first approach, results of model calculations for binary nucleation of H_2SO_4 and water from Pirjola *et al.* [6] were used to see if they predicted the patterns seen in the number concentration. Pirjola's work correlated the key variables of preexisting surface area, OH concentration and SO_2 concentration with an increase in the total number concentration due to the nucleation and growth of new particles due to sulfuric acid and water. The estimated nucleation strength was a poor predictor of observed nucleation activity. However, that is not to say that SO_2 oxidation is not involved in nucleation. In a simple multiple linear regression of nuclei mode particles against 17 gas phase, particle phase, and meteorological variables, the product of ultraviolet radiation and SO_2 concentration was the strongest predictor, indicating that SO_2 oxidation is important to observed nucleation, but perhaps with a quantitatively different relation than proposed by Pirjola.

The second approach involved sampling and analysis of freshly formed particle in a Laser Ablation Mass Spectrometry system (LAMMS) [7]. Particles of around 20 nm were concentrated using a newly developed ultrafine particle concentrator [8] and then selected using the aerodynamic lens system of the LAMMS. This experiment, performed on multiple days with nucleation in March 2002, indicated mainly carbonaceous material in the aerosols. However, the LAMMS sensitivity to sulfur species is very low. This indicates that condensation of secondary organic aerosol is an important growth mechanism for the new particles.

The third approach was to evaluate the hygroscopic growth of fresh particles by comparing size distributions measured at different relative humidities during nucleation events. In one nucleation event, particles were sampled alternately at dry (10%) and 43% relative humidity, and showed no hygroscopic growth. On another day, particles were sampled at dry and $55 \pm 5\%$ relative humidity and showed modest hygroscopic growth, consistent with a mixture of more hygroscopic inorganic compounds and less hygroscopic organic compounds. The hygroscopic properties of the nuclei were investigated in a targeted experiment where the relative humidity was varied between four points, yielding a hygroscopic growth curve for the fresh particles. This is shown in Figure 13 and indicates mixed particle composition.

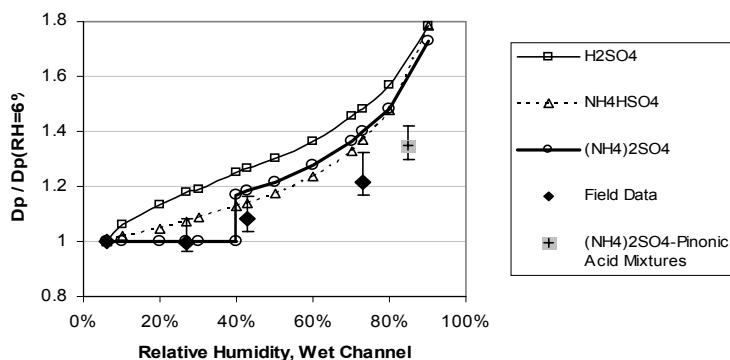


Figure 13. Hygroscopic growth of fine particles (<30nm) during nucleation event. Data for ammonium sulfate-pinonic acid mixtures represents range of hygroscopic growth for 50 nm dry particles in ratios of 20:80, 50:50, and 80:20 salt:organic acid from Cruz and Pandis [9].

Conclusions

Field data from the Pittsburgh Air Quality Study has improved understanding of several important phenomena regarding regional particulate matter. First, regional sources are the dominant contributor to particulate matter in the Pittsburgh region. Second, organic aerosol concentrations averaged approximately 8 $\mu\text{g}/\text{m}^3$ during summer of 2001 and 5 $\mu\text{g}/\text{m}^3$ during the winter of 2001. On average, $30 \pm 20\%$ of the organic aerosol is secondary in summertime, while in winter the secondary organic aerosol is less than 20% of the total OC. Third, nucleation occurred frequently (30-50% of study days) and contributed significantly to the overall number concentration and size distribution. Preliminary results from single particle mass spectrometry and hygroscopic growth experiments show that 30 nm fresh particles contain both inorganic and organic compounds.

Acknowledgement

This work would not have been without the contributions of a large number of graduate and undergraduate students at Carnegie Mellon University and the many collaborators working on the Pittsburgh Air Quality Study. In particular this paper highlights the research of Charles Stanier, Juan Cabada, and R. Subramanian. Thanks to Timothy Raymond and Wei Tang for their work collecting samples at the satellite sites. The Pittsburgh Air Quality Study is supported by the US Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017 and by the US EPA through the Supersites Program. This paper has not been subject to EPA's required peer and policy review and therefore does not necessarily reflect the views of the EPA, and no official endorsement should be inferred.

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